NAS 12-688

THE REDUCTION OF CHLORINE ON CARBON IN $AlCl_3$-KCl-NaCl MELTS

by

Gerhard L. Holleck

Tyco Laboratories, Inc.
Bear Hill
Waltham, Massachusetts 02154

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ABSTRACT

Using a rotating vitreous carbon disk electrode, the kinetic parameters for chlorine reduction in an $AlCl_3$-KCl-NaCl (57.5-12.5-30 mol %) melt were determined. It was found that the reduction of chlorine occurs according to the paths:

$$Cl_2 + e^- \rightleftharpoons Cl^- + Cl_{ads}$$

$$Cl_{ads} + e^- \rightleftharpoons Cl^-$$

with the first step being most probably rate determining. The apparent exchange currents were $(1 \pm 0.15)10^{-4}$ A/cm^2 at 130 °C and $(2.1 \pm 0.3)10^{-4}$ A/cm^2 at 150.6 °C.

The electrochemical reduction of chlorine in molten salts is of general interest to the development of high energy density batteries. One such proposed battery system is based on an aluminum anode and a chlorine cathode in a low melting aluminum chloride-alkali chloride eutectic.[1] In a previous paper, we have dealt with the behavior of the aluminum electrode in $AlCl_3$-KCl-NaCl melts.[2] This work is concerned with the kinetics of chlorine reduction in such melts.

Despite the use of the chlorine electrode for a number of years as a reference electrode in fused slats,[3] kinetic and mechanistic studies have been quite limited. Treadwell and Terebessi conducted EMF studies of the cell Al/ $AlCl_3$-KCl-NaCl/Cl_2.[4] Skundin, et al., carried out studies of chlorine reduction in $AlCl_3$-KCl-NaCl melts at 100 - 150 °C on Pt and Ir electrodes using linear sweep voltammetry.[5] They estimated an exchange current of 10^{-4} A/cm^2 with no evidence of surface film formation. Drossbach and Piontelli both investigated the evolution of chlorine from chloride melts and found small polarizations.[6, 7] The evolution of chlorine from LiCl-KCl melts in the temperature range of 425 - 650 °C was found to be resistance controlled primarily due to the gas film present on the electrode surface.[8] Triaca, et al., found that the dissolution of chlorine on graphite in molten LiCl was diffusion controlled at higher current densities which precluded mechanistic conclusions.[9] Other studies of the reduction of chlorine on graphite electrodes in molten salts have been made by Ivanovskii, et al.,[10] Trusov and Borisova,[11] and Swinkels.[12]

In preliminary studies, we found that graphite-containing samples showed considerable swelling and disintegration in aluminum chloride-alkali chloride melts. Vitreous carbon which did not show any attack was chosen as a suitable electrode material for kinetic studies of chlorine reduction on carbon surfaces in $AlCl_3$-KCl-NaCl melts using the rotating disk electrode technique.

Experimental:

The rotating disk arrangement consisted of a sturdy stand on which a 1/15-hp Bodine motor and a precision ball bearing for the 0.25-in. rotating shaft

were mounted. The motor speed was controlled by a Minarik speed control (SL-52). The coupling of the motor and the electrode shaft was accomplished by a nonslip belt. The rotation rate of the electrode was continuously monitored by the frequency modulation resulting from magnetic coupling of an electromagnet with an iron gear mounted on the rotating shaft. This signal was amplified and displayed on a frequency counter. Electrical contact to the disk electrode was accomplished through a mercury pool in the top of the rotating shaft.

The electrochemical cell was made of a 50-mm O-ring joint with a 30-mm-thick Teflon cover. The Teflon cover contained tapered holes to accommodate a liquid seal in the center with a 29/40 standard tapered joint surrounded by four 10/30 joints for the gas inlet and outlet as well as the counter and reference electrodes. A Teflon bell was fixed to the rotating shaft (Fig. 1). Silicone oil with a low vapor pressure was used as sealant liquid.

The rotating electrode consisted of a vitreous carbon rod (3-mm diameter, from Atomergic Chemicals Corporation) press fitted into hot Teflon. Details of the electrode construction are shown in Fig. 1. A vitreous carbon rod was used as counterelectrode and an Al electrode in the same melt, but in a separate compartment, served as reference electrode. The electrochemical cell was thermostatted by a stirred silicone oil bath controlled to ±0.2 °C by a Matheson Lab Stat proportional temperature control unit and a two-stage heating arrangement. The chlorine from a gas cylinder was passed through a trap filled with molecular sieves (Linde No. 5A) which had been dried at 375 °C under dry argon overnight before entering the cell.

The experiments were conducted in the $AlCl_3$-KCl-NaCl melt (57.5-12.5-30 mol %) at 130 and 150.6 °C. The purification of $AlCl_3$ and the preparation of the melts has been described in detail elsewhere.[2] Before introducing Cl_2 gas into the cell, cyclic voltammograms were taken at the carbon disk electrode (these showed no detectable faradayic background current). Following this, the argon was replaced by Cl_2, and a slow flow of Cl_2 was maintained above the melt surface. The progress of melt saturation was monitored by measuring the

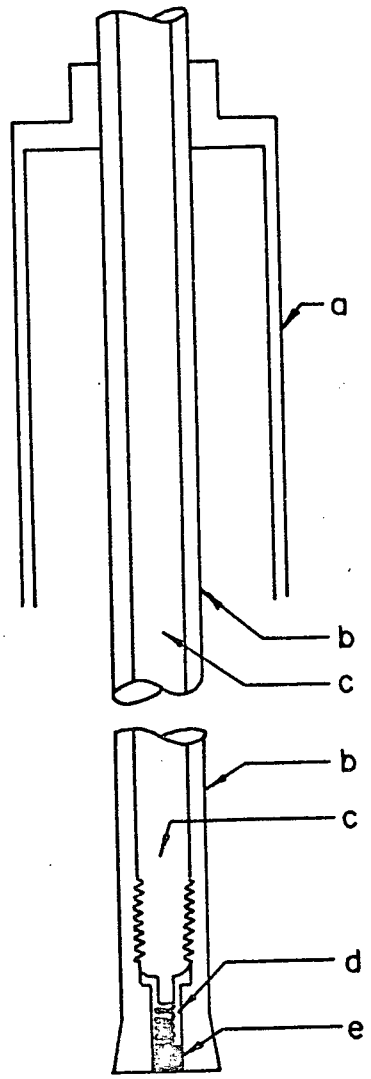


Fig. 1. Schematic diagram of rotating disk electrode (a) Teflon bell for liquid seal, (b) Teflon, (c) stainless steel shaft, (d) contact spring, (e) vitreous carbon

increase of the limiting current of the Cl_2 reduction with time at constant rotation speeds. Generally, the stirred melt was saturated with Cl_2 after 25 to 30 min.

Results:

The open circuit potentials at 130 and 150 °C were 2.10 and 2.06 V, respectively. A typical current-voltage curve at 130 °C, at a sweep rate of 200 mV/min, is shown in Fig. 2. A slight hysteresis was observed between the forward and the backward sweep. The hysteresis at low current densities was independent of rotation rate, whereas the differences between the forward and backward sweeps at, or close to, the limiting current region increased with increasing rotation rate. Fig. 3 shows the change of current with time at constant potential at a rotation rate of 30 rps.

Besides the buildup of the diffusion layer, we observed a relatively slow current decay which is clearly potential dependent. It is largest at 1.2 V, in keeping with the current-voltage curves, and reaches a steady value after about 3 min. At 0.8 and 1.7 V, steady-state values are more quickly established. This and the reproducibility of the current-voltage sweeps after returning to the open circuit potential suggest a potential dependent inhibition. The exact cause of this behavior is not yet known. However, it seems most likely that some melt impurity is involved.

Limiting currents of chlorine reduction as a function of rotation rate are shown in Fig. 4. The data show the linear relationship predicted for a mass transfer controlled reaction:[13]

$$i_L = A\, n\, F D^{2/3} \nu^{-1/6} \omega^{1/2} C_o$$

(where A = constant, D = diffusion coefficient, C_o = concentration of the electroactive species, ν = viscosity, $\omega = 2\pi N$ where N = rotation rate.

The limiting currents obtained from cyclic current-voltage sweeps at 3.3 V/min follow a straight line with a slope of 1.48 $mA/cm^2 \omega^{1/2}$. The limit-

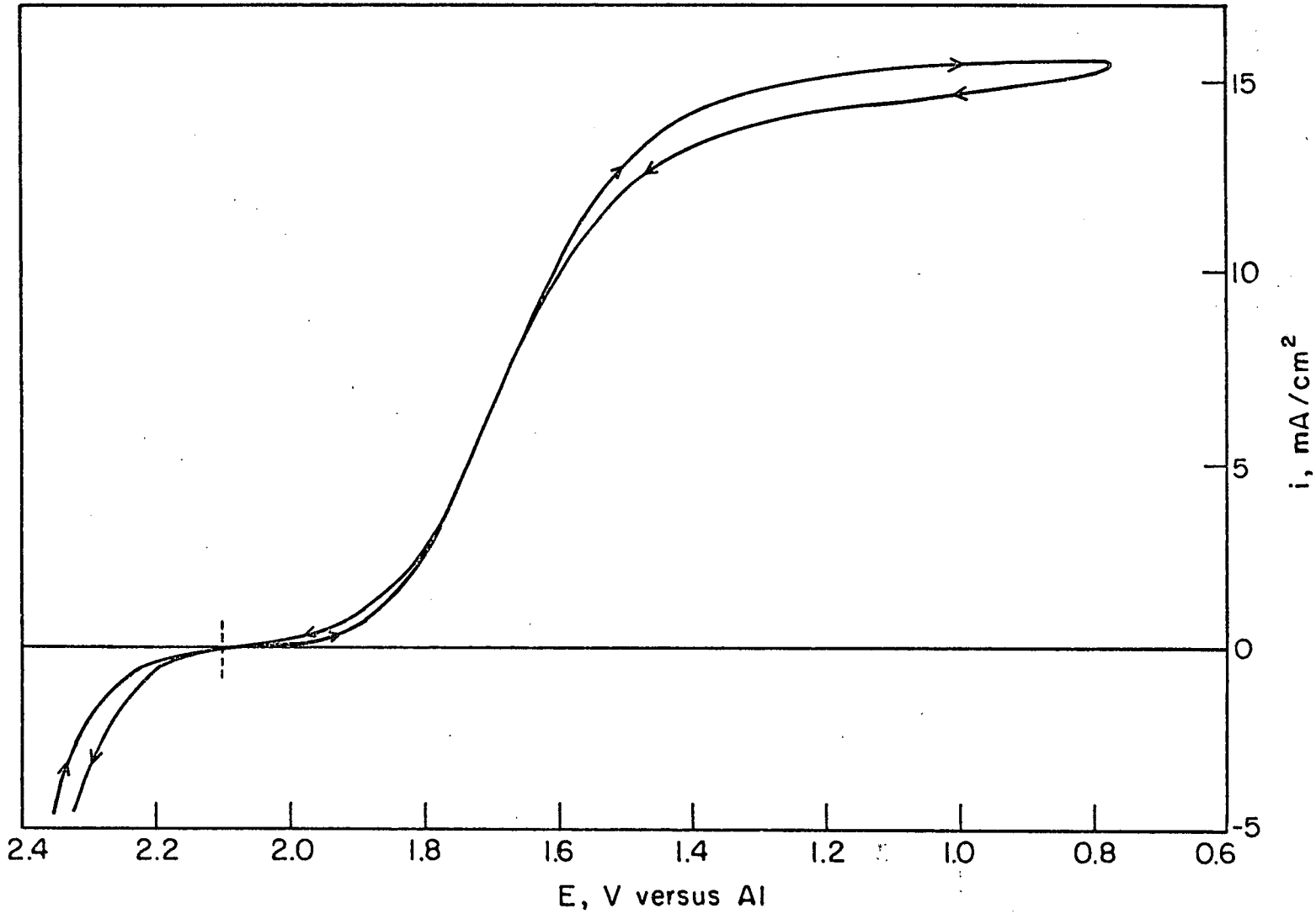


Fig. 2. Reduction of Cl_2 at rotating carbon disk electrode in $AlCl_3$-KCl-NaCl (57.5-12.5-30 mol %) at 130 °C, 20.8 rps, and 200 mV/min

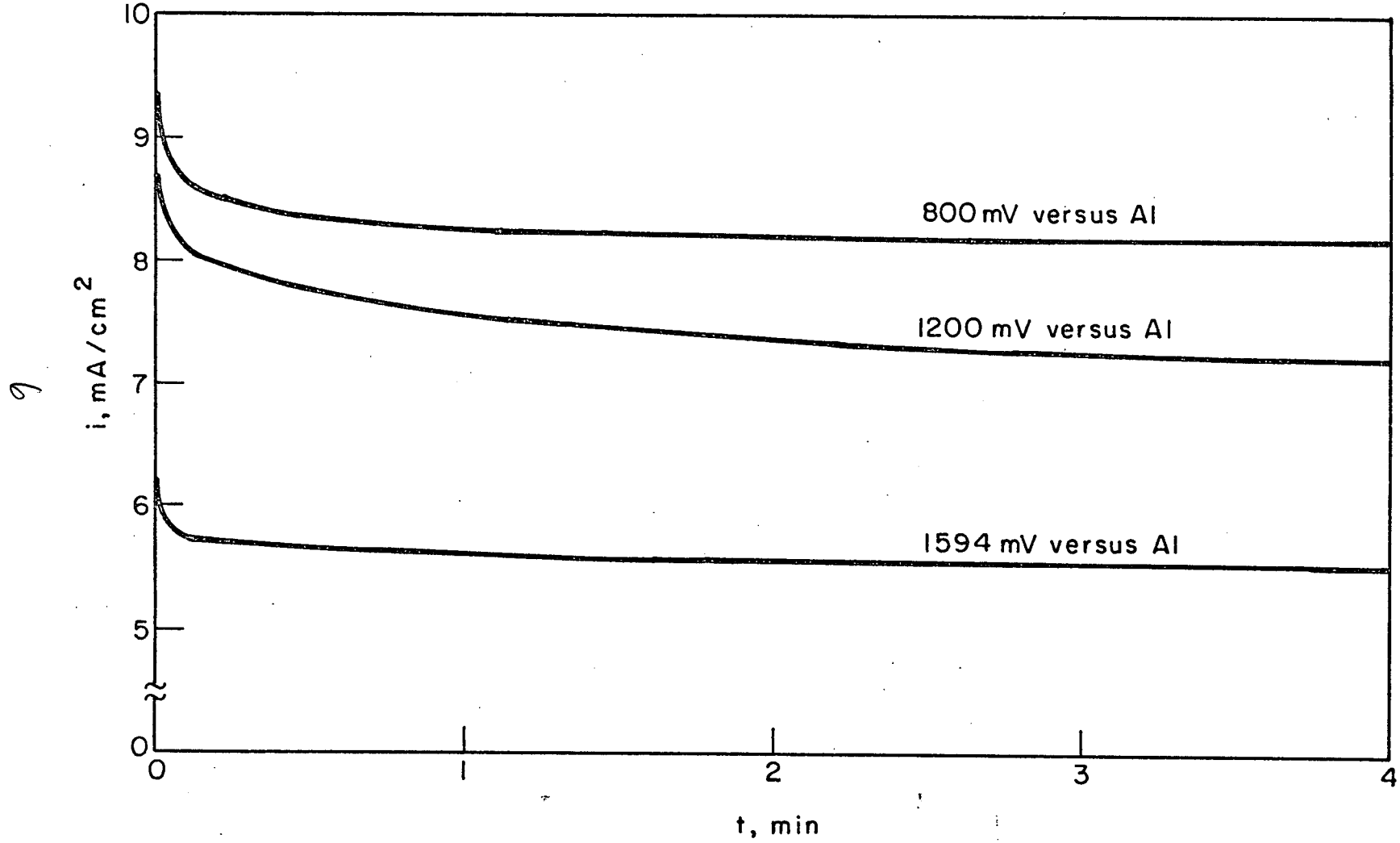
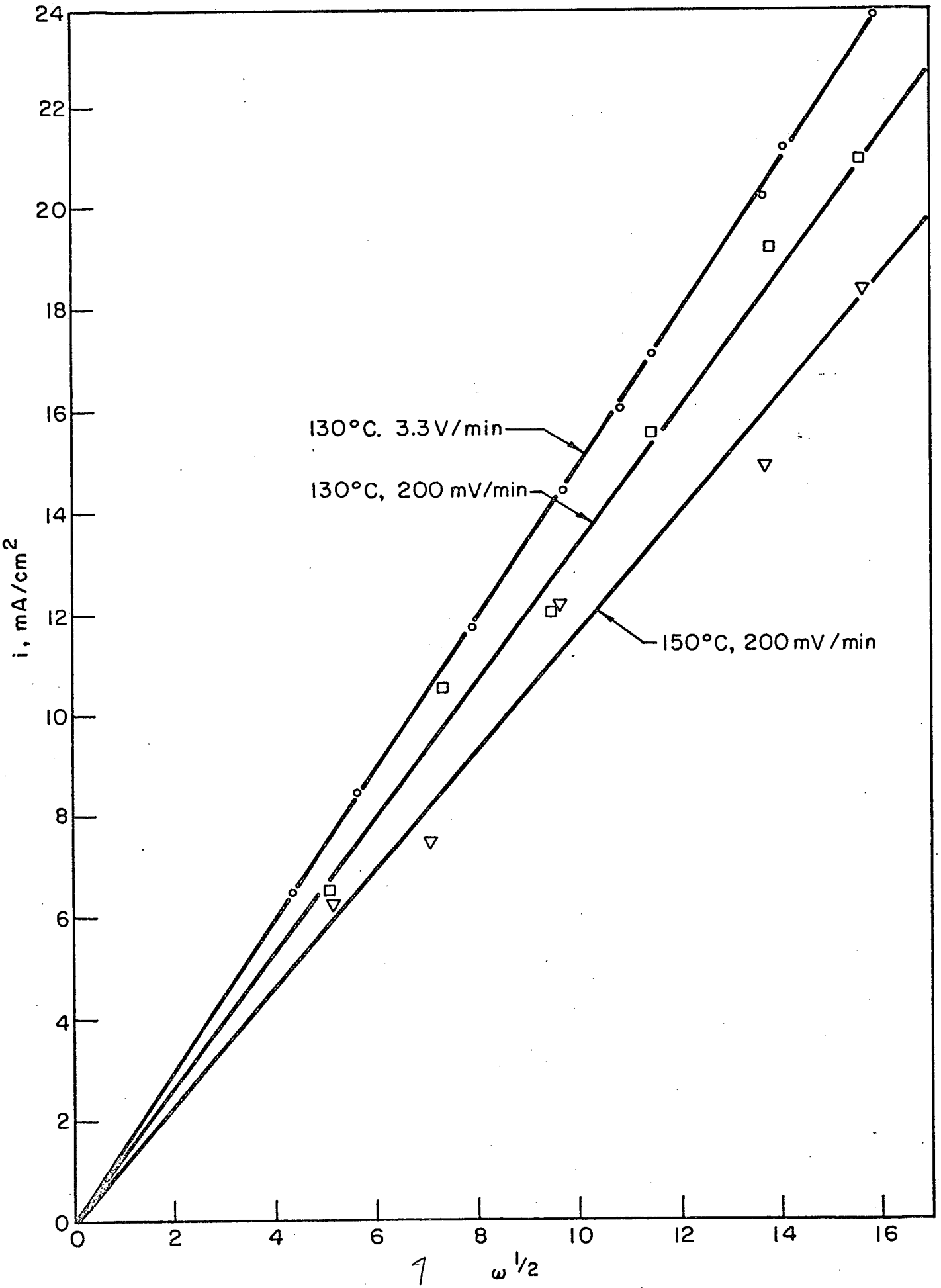


Fig. 3. Decay of Cl_2 reduction current with time upon potentiostatic steps to various potentials (versus Al) at the rotating disk electrode in $AlCl_3$-KCl-NaCl (57.5-12.5-30 mol %) at 130 °C and 30 rps

Fig. 4. Limiting currents for Cl_2 reduction versus rotation rate at carbon electrode in $AlCl_3$-KCl-NaCl (57.5-12.5-30 mol %)



ing current values from the slow current-voltage sweeps show larger scatter and a somewhat smaller slope (1.37 $mA/cm^2\omega^{1/2}$), reflecting the slow current decay mentioned above. At 150.6 °C, a slightly smaller slope resulted, indicating that the increase in the factor $D^{2/3}\nu^{-1/6}C_o$ is overcompensated by a decrease of the Cl_2 solubility. The transport parameter ($D^{2/3}\nu^{-1/6}C_o$) is approximately 1.4×10^{-8} [$(cm^2/sec)^{2/3}$ $poise^{-1/6}$ mol/cm^3] at 130 °C from which the chlorine solubility can be estimated to about 5 mmol/ℓ.

Fig. 5 shows the current potential data in a diffusion corrected Tafel plot of the form:

$$\eta = \frac{2.3\ RT}{\beta z F} \log i_o - \frac{2.3\ RT}{\beta z F} \log \frac{i}{1 - (i/i_L)} \qquad (1)$$

where the symbols have their usual meaning. It is applicable for a reaction with a simple rate determining step and of first order with respect to the difusing species.

The experimental data in Fig. 5 show good Tafel behavior up to high overvoltages. The main Tafel slope was 200 mV at 130 °C and 210 mV at 150.6 °C. This suggests a one-electron transfer in the rate determining step with $\beta = 0.4$. At lower overvoltages (between $\eta = 50$ and 250 mV), the current of the cathodic going sweep follows a Tafel line with a decreased slope (130 mV/decade). On the returning potential sweep, no change in Tafel slope occurred. The exchange currents for chlorine reduction obtained from the main Tafel region were $(1.0 \pm 0.15)10^{-4}$ A/cm^2 at 130 °C and $(2.1 \pm 0.3)10^{-4}$ A/cm^2 at 150.6 °C with an activation energy of 12 kcal/mol.

The rotating disk electrode offers a particular advantage in determining the reaction order with respect to the reactants and products by studying the effect of rotation rate at a fixed potential as was illustrated by Frumkin and Aikazyan.[14]

For a rate determining step, $q\ O + z\ e^- \rightarrow R$, we can write:

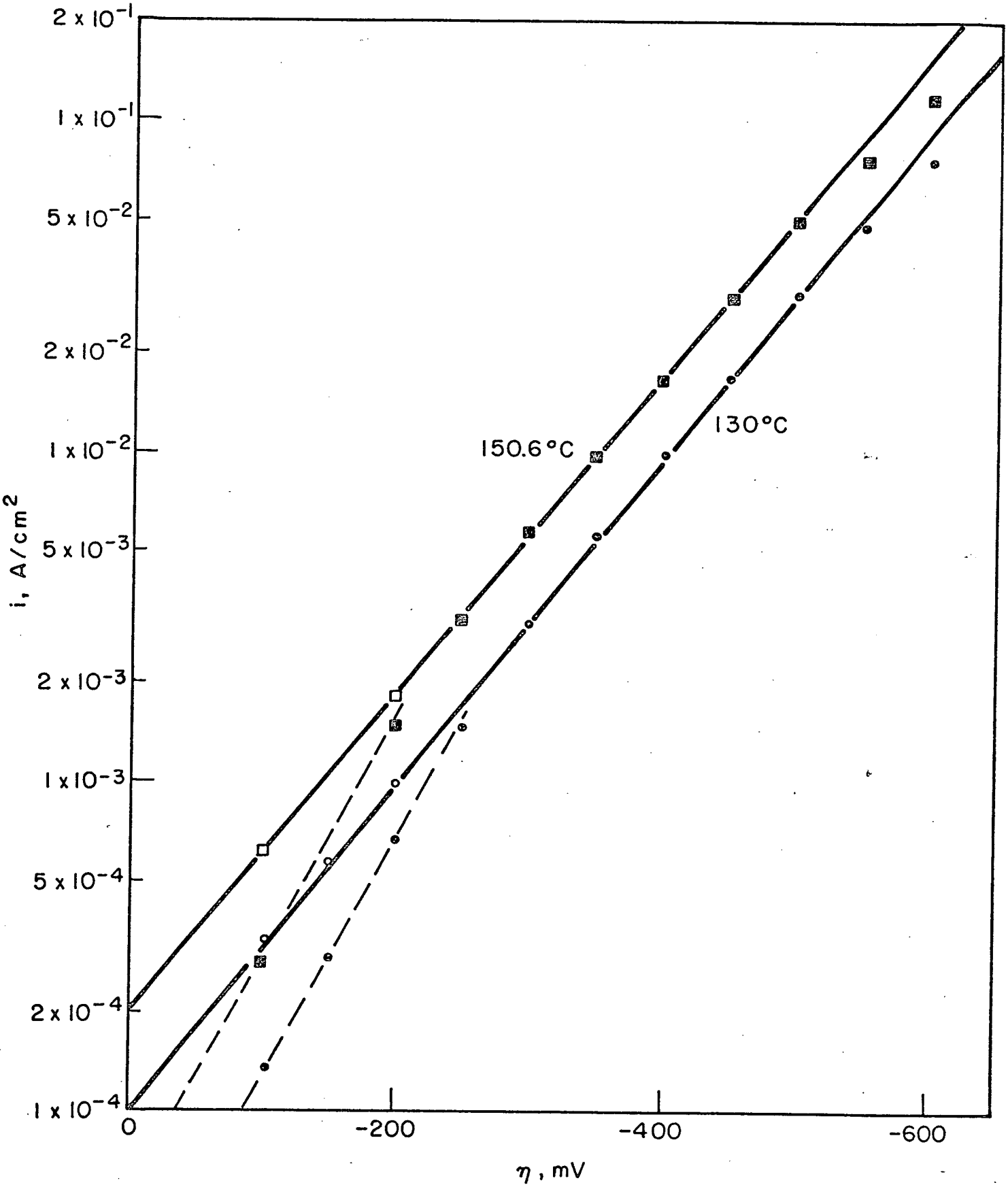


Fig. 5. Diffusion corrected Tafel plots for Cl_2 reduction, $AlCl_3$-KCl-NaCl (57.5-12.5-30 mol %) (open symbols at low η represent returning sweep)

$$\frac{i}{i^*} = \frac{C_o^o}{C_o^\infty} = \left(1 - \frac{i}{i_{L,c}}\right)^q \qquad (2)$$

where i = measured current, i^* = activation controlled current, C_o^∞ and C_o^o are the concentration of species O in the bulk of the electrolyte and at the electrode surface respectively, and q = reaction order with respect to the diffusion species.

With q = 1, Eq. (2) converts to:

$$\frac{1}{i} = \frac{1}{i^*} + \frac{1}{K\,\omega^{1/2}} \qquad (3)$$

(K is the scope of the plot i_L versus $\omega^{1/2}$) while q = 1/2 (for instance) results in:

$$i^2 = (i^*)^2 - \frac{(i^*)^2}{K}\,\frac{i}{\omega^{1/2}} \qquad (4)$$

A typical plot of 1/i versus $1/\omega^{1/2}$ according to Eq. (3) is shown in Fig. 6. The linear relationship of the experimental data suggest a reaction order of one. From the intercept at 1/i = 0, $i^* = 80\ \mu A/cm^2$ was calculated as found in the Tafel plots. The slope $1/K = 780\ cm^2\omega^{1/2}/A$ is in good agreement with K from Fig. 4.

From the initial slope of galvanostatic potential-time curves close to the open circuit potential, the double layer capacity was determined to 110 ± 15 $\mu F/cm^2$, which is larger than the 20 to 30 $\mu F/cm^2$ one would normally expect to find. The larger capacity values are most likely due to an increased roughness factor of the electrode and/or an adsorption capacitance.

Discussion:

The overall reaction:

$$Cl_2 + 2\,e^- \rightleftharpoons 2\,Cl^-$$

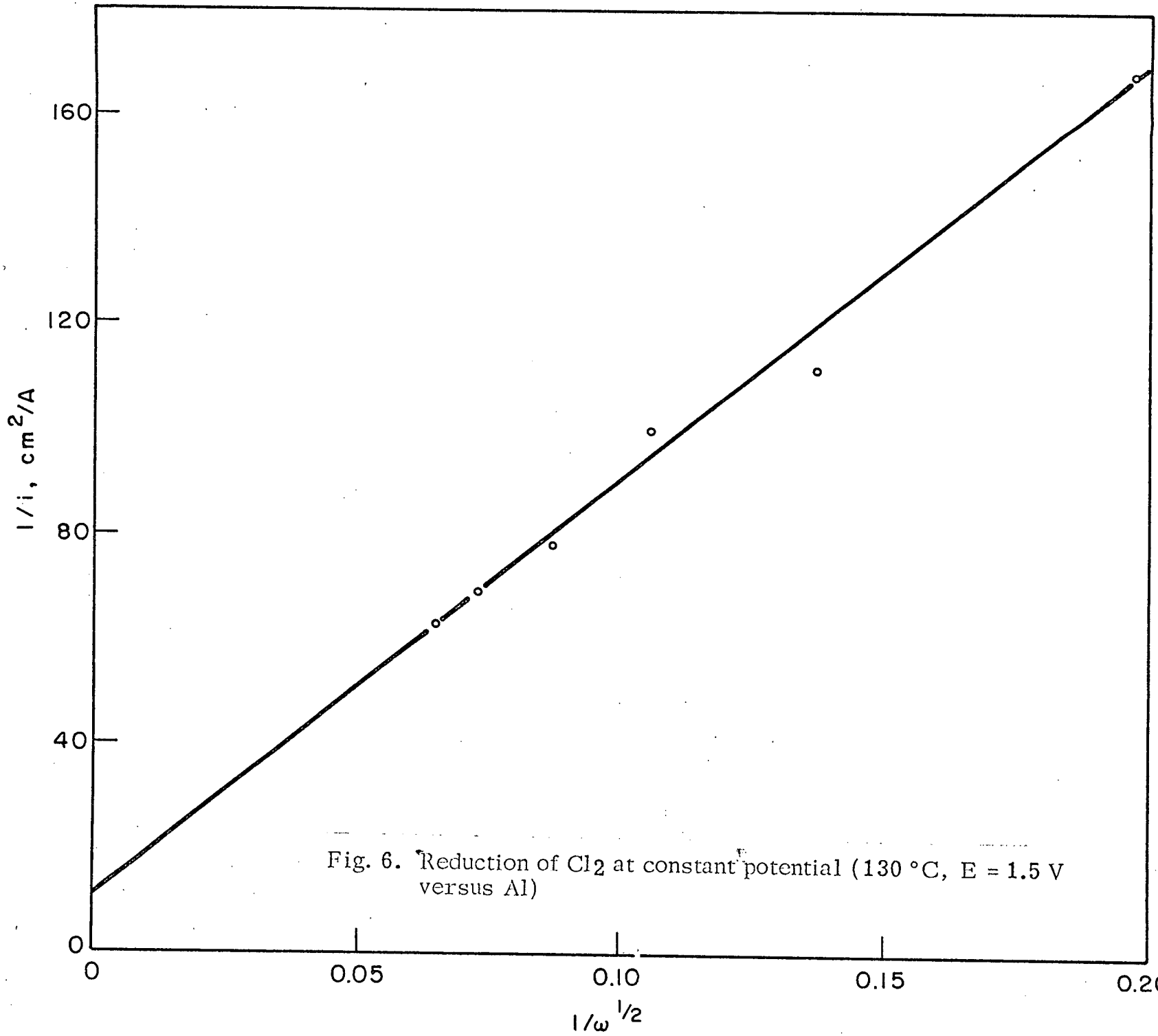


Fig. 6. Reduction of Cl_2 at constant potential (130 °C, E = 1.5 V versus Al)

can occur according to two paths:

$$\text{(a)}\quad Cl_2 + e^- \rightleftharpoons Cl^- + Cl_{ads}$$

1

$$\text{(b)}\quad Cl_{ads} + e^- \rightleftharpoons Cl^-$$

$$\text{(a)}\quad Cl_2 \rightleftharpoons 2\,Cl_{ads}$$

2

$$\text{(b)}\quad Cl_{ads} + e^- \rightleftharpoons Cl^-$$

The fact that the reaction for the chlorine reduction was found to be first order excludes the second path.

A calculation of the theoretical Tafel slopes of the first path, depending on whether step (a) or step (b) is rate determining results in the following values.

	Langmuir adsorption		Temkin adsorption	
Rate determining	$\theta \to 0$	$\theta \to 1$	nonactivated	activated
1a	$-2RT/F$	$-2RT/3F$	$-2RT/F$ or $-2RT/3F$	$-RT/F$
1b	$-2RT/3F$	$-2RT/F$	$2RT/3F$	$-RT/F$

The experimentally determined main Tafel slope was 2.5 RT/F. The above table shows that the value for the Tafel slope alone is not sufficient to distinguish between steps (a) or (b). The measured slope could reflect a rate-determining step according to 1a at low coverage of the electrode or according to 1b at large electrode coverage. Thus additional information concerning the electrode coverage would be required. Studies of the mechanism of chlorine evolution on graphite[9] in molten lithium chloride suggest as the rate determining step the combination of chlorine atoms on a surface with appreciable coverage.

In fact, when scanning the rotating carbon electrode from the region of chlorine evolution to more cathodic potentials, one indeed observes up to overvoltages of 250 mV a lower Tafel slope which changes to 2RT/F at higher overvoltages probably indicating the change from an intermediate to low coverage. On the anodic going sweep, this low coverage is maintained until reaching anodic potentials.

Thus, we can conclude that the chlorine reduction on vitreous carbon in $AlCl_3$-KCl-NaCl melts occurs according to path 1 with step 1a being most probably rate determining at higher polarizations with a low chlorine coverage on the electrode.

ACKNOWLEDGEMENT

The author wishes to thank Dr. José Giner for many helpful discussions.

This work was supported by the Electronics Research Center, National Aeronautics and Space Administration under Contract No. NAS-12-688.

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